Thickness-dependent magnetic properties of oxygen-deficient EuO

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We have studied how the magnetic properties of oxygen-deficient EuO sputtered thin films vary as a function of thickness. The magnetic moment, measured by polarized neutron reflectometry, and the Curie temperature are found to decrease with reducing thickness. Our results indicate that the reduced number of nearest neighbors, band bending and the partial depopulation of the electronic states that carry the spins associated with the 4f orbitals of Eu are all contributing factors in the surface-induced change of the magnetic properties of EuO$_{1-x}$.

Electron-doped EuO is a semiconductor which undergoes a simultaneous ferromagnetic and insulating-conducting phase transition, across which the resistivity drops by 8 to 13 orders of magnitude [1, 2] and the conduction electrons become nearly 100 % spin polarized [3, 4], making EuO a strong candidate for efficient spin filtering [5, 6]. Electron doping increases the Curie temperature of EuO thin films to above 200 K [7] from 70 K for undoped EuO, and also increases the magnetic moment up to 7.13 μ_B from the intrinsic value of 7 μ_B [6]. This is due to the enhanced, conduction-electron-mediated RKKY coupling between the Eu 4f spins [8, 9]. In thin films and interfaces these fundamental magnetic properties can also be influenced by additional factors, such as surface-induced modification of the crystalline environment and of the band structure [10] as well as magnetic proximity effects [11–13]. These interface effects have been studied experimentally mainly in 3d systems, be they itinerant ferromagnets [10] or transition metal oxides [14, 15], while interfaces of the 4f compound EuO have only been analyzed theoretically [16, 17].

In this Letter we study systematically the Curie temperature $T_C(d)$ and magnetic moment per Eu atom, $m(d)$, in dependence of the thickness d of ultrathin layers of oxygen-deficient EuO$_{1-x}$ in the thickness range from 2 to 6 nm, interfaced with Pt capping layers. Our previous investigation in the range from 7 to 12 nm for various O-defect concentrations [6] did not show a thickness dependent variation of the magnetic properties relative to bulk samples. However, in the ultrathin layers of the present work we find a systematic reduction of both $T_C(d)$ and $m(d)$ with decreasing d. Our analysis shows that band bending and the reduced number of nearest neighbors at the interface cause the thickness-dependent functionality of $T_C(d)$ and $m(d)$, due to the increased relative importance of the interface. We are then able to estimate the charge screening

length and the spatial extension of the RKKY interaction in EuO$_{1-x}$.

Thin films of EuO$_{1-x}$ with x=4% were deposited by co-sputtering of Eu$_2$O$_3$ and Eu on Si substrates with a Pt buffer and capping layer of 10 nm each, as described in Ref. [6]. The samples were characterized by superconducting quantum interference device (SQUID), x-ray reflectometry (XRR) and polarized neutron reflectometry (PNR) on the CRISP beamline at ISIS [18], following the same analysis as carried out in Ref. [6]. Since EuO is unstable towards phase separation, i.e. towards formation of elemental Eu and of the nonmagnetic, chemically stable oxide Eu$_2$O$_3$, it is crucial to determine the number density of magnetic Eu atoms in order to measure the magnetic moment per Eu atom in the EuO phase, $m(d)$. This is achieved by fitting the PNR data to a theoretical model with the following parameters: neutron scattering length, neutron absorption, atom number density, fraction of nonmagnetic phases, magnetic film thickness d, and total magnetic moment of each layer, see Ref. [6]. The PNR data and theoretical fits are shown in Fig. 1, where the reduction in peak spacing and the progressive separation of the spin up and spin down curves track the increase in thickness. The other fit parameters were found to be the same as for the thicker samples previously measured [6]. The samples were polycrystalline and the interlayer roughness was estimated to be about 0.6 nm (rms amplitude).

Curie temperature. The thickness-dependent T_C for thin films of EuO$_{0.96}$ in the thickness range between 2 and 40 nm is plotted in Fig. 2, normalized to the respective bulk value T_C^∞, together with data for EuO taken from Refs. [19, 20]. The reduction of T$_C$ for stoichiometric, i.e. insulating EuO can be understood qualitatively by describing the Eu 4f subsystem within a spin $S = 7/2$ Heisenberg model with an effective nearest-neighbor spin exchange coupling J [9]. In mean field theory $T_C^{(MF)} = ZJ/4k_B$,
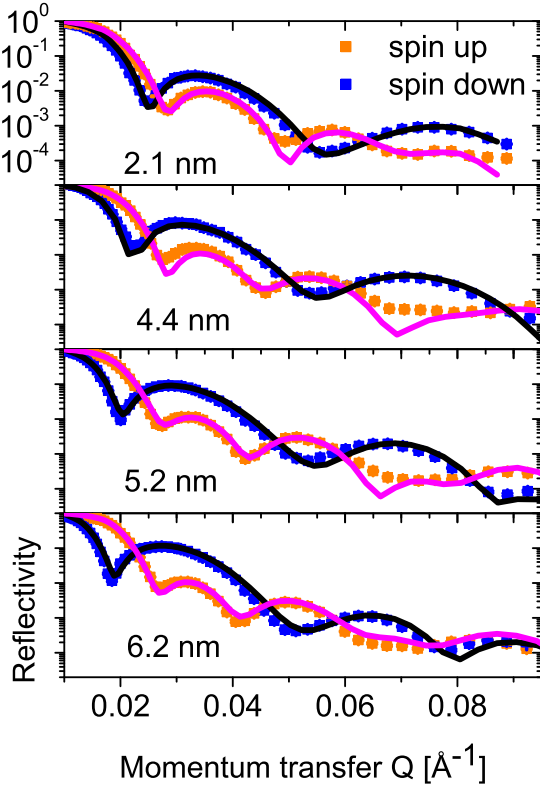
FIG. 1: (Color online) PNR data (datapoints) and fit (lines) for varying thickness, d_{PNR}=2.1, 4.4, 5.2 and 6.2 nm. Data taken at T=5 K with an applied magnetic field of 3 kOe.

that is proportional to the number of nearest neighbors Z, which is reduced from $Z_b = 12$ in the bulk fcc lattice of EuO to $Z_i = 8$ at the interface (J is the spin exchange coupling and k_B the Boltzmann constant). Thus, averaging Z over a film with n atomic layers (a monolayer of EuO is 0.25 nm) and two interfaces leads to a reduction in T_C:

$$T_C^{(MF)} = \frac{2Z_i + (n-2)Z_b}{n} \frac{J}{4k_B}, \quad n \geq 2. \quad (1)$$

This expression, after normalization to T_C^∞ free of adjustable parameters, is shown in Fig. 2 (red curve). We attribute the stronger experimental T_C suppression to the fact that in EuO next-nearest-neighbor couplings are not negligible [9] and that in thin films fluctuations, not included in mean field theory, become increasingly important.

For oxygen-deficient EuO$_{0.96}$ the simple analysis in terms of a reduced number of neighbors is not sufficient due to the additional exchange interaction pathway mediated by the occupied conduction-band states, that is long-range RKKY. While the the RKKY interaction causes an increase in the absolute value of T_C relative to undoped EuO [9], it also has the consequence of making the films more susceptible to surface effects: the reduction in T_C extends up to significantly larger thicknesses compared to undoped EuO. We can extract an experimental estimate for the range ξ of the effective spin coupling by fitting

the experimental data with a phenomenological Fermi-like function, $T_C/T_C^\infty = [exp(1 - d/\xi) + 1]^{-1}$, which describes both the T_C saturation for large d and the approximately linear T_C suppression for small d, by a single length scale ξ. The best fits yield an effective range of $\xi \approx 1.2$ nm for $x = 0\%$ and $\xi \approx 9$ nm for $x = 4\%$. We also note that we have attempted to reproduce the reduction in T_C for EuO$_{0.96}$ by performing mean field calculations for a layered Heisenberg model with an additional, RKKY-induced, effective spin exchange coupling $J'(z) = J_0 \cos(2k_F z)/z$, cut off at the thermal length, where z is the distance between two spins perpendicular to the interface. We found a T_C reduction for films up to $d = 40$ nm (not shown) in qualitative agreement with experiment; However, it was not possible to reproduce the experimental $T_C(d)$ curve quantitatively by a spatially constant strength J_0 of the RKKY-induced interaction. We attribute this to our finding, which will be discussed below in the context of the magnetic moment data, that a substantial conduction band bending occurs near the interfaces, leading to spatially dependent modifications of the RKKY interaction.

Magnetic moment reduction. The magnetic moment per Eu atom (measured by PNR at 5 K, c.f. Fig. 1) and thickness (measured by PNR and XRR) for magnetically saturated EuO$_{0.96}$ films are indicated in Table I (the data for the 11.7 nm sample is taken from Ref. [6]). The expected magnetic moment for EuO$_{0.96}$ is 7.08 μ_B/Eu atom [6]. As seen in Fig. 3 there is a marked, approximately linear reduction of the magnetic moment with decreasing thickness, by up

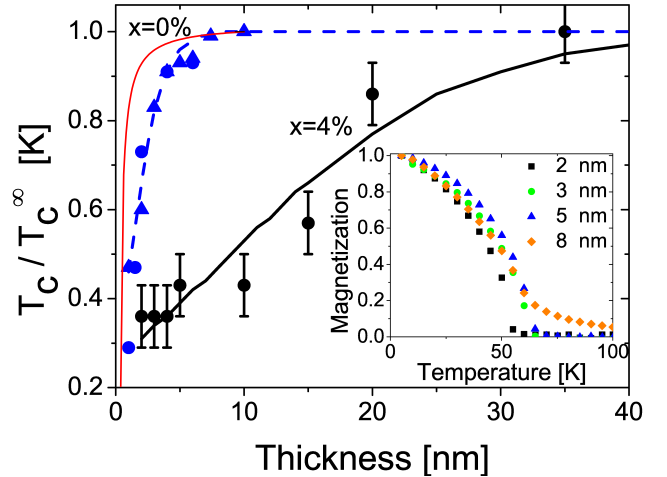FIG. 2: (Color online) T_C / T_C^∞ of EuO$_{1-x}$ for varying thickness, for x=4% (black circles). The data for x=0% (blue triangles and circles) is taken from Refs. [19, 20]. Above 40 nm T_C for x=4% saturates to 140 K (normalized value of unity, datapoints not shown). The red curve represents Eq. (1) normalized to its value for the largest experimentally considered thickness (10 nm). The black and blue fit lines are described in the text. The inset shows the magnetization as a function of temperature for increasing thickness, with a 50 Oe applied field. Each magnetization curve is normalized to its own value at 5 K.

TABLE I: Magnetic moment of $EuO_{0.96}$ with varying thickness.

d_{PNR} (nm)	d_{XRR} (nm)	$\mu(B)$ PNR ($\pm 0.09\,\mu_B$) (μ_B/Eu atom)
2.1	1.8	6.41
4.4	4.5	6.80
5.2	5.5	6.99
6.2	5.8	7.08
11.7	12.3	7.07

to 9% for the 2.1 nm sample. We note that a decreased value for the moment of ultra thin films of stoichiometric EuO is visible in the data reported by Santos *et al.* [19], which display a monotonic decrease of the magnetic moment with decreasing thickness [28].

To understand the moment reduction, several effects must be considered. In contrast to the T_C suppression, the moment reduction cannot be understood in terms of surface-reduced effective exchange couplings, since the saturated ferromagnetic moment is independent of the coupling. Further, we can exclude that the origin of the moment reduction lies in a renormalization of the Landé factor g near the interface, to a value significantly below the bulk one: In saturated thicker (bulk-like) films of EuO_{1-x} with x=4% the observed magnetic moment per Eu atom is $m = 7.08\,\mu_B$ (c.f. Table I), i.e. equal to the combined maximum spin moment of the Eu $4f$ electrons and of the two dopant electrons per O-defect, $m = g\,(7/2 + x)\,\mu_B$, where the Landé factor assumes its vacuum value, $g = 2$. This indicates that orbital, band structure or many-body effects do not play a significant role for the g-factor. Hence we do not expect that g is modified due to orbital quenching or a change of band structure near the interface. Moreover, the Landé factor of Pt has consistently been reported to be larger than 2 [21], so that we don't expect a reduction of g in EuO_{1-x} due to proximity to the Pt capping layer. The moment reduction in thin EuO_{1-x} films cannot thus be explained by a reduction of the g-factor. Another factor to consider is that the $4f$ orbitals of EuO have been reported to be susceptible to pinning from the local crystalline environment [22, 23]; this could cause a reduction of the moment. However, such surface pinning would result in a strongly non-linear thickness dependence of the average moment, with a functionality of the type given by Eq. (1) (red curve in Fig. 2). Since this fails to fit the measured behavior which is linear in the thickness range of $d = 2 - 6$ nm, as seen in Fig. 3, we can exclude pinning effects as the primary cause of the observed behavior.

The last factor we consider in our analysis, and the one with definite support from the experimental data, is the large difference between the work functions Φ of EuO_{1-x} ($\Phi_{EuO} \lesssim 1$ eV [24]) and of the Pt capping layer ($\Phi_{Pt} \approx 5.6$ eV). One expects a significant electron transfer from the EuO_{1-x} film to the Pt layer, resulting in an interface potential $V(z)$, where z is the vertical distance from the

interface. Since the difference between the work functions, $\Phi_{Pt} - \Phi_{EuO} \approx 4.6$ eV, is larger than the binding energy of the Eu $4f$ band, whose upper edge lies about 1.2 eV below the conduction band [3, 24], the charge transfer will involve not only the bulk conduction electrons, but also the $4f$ electrons, i.e. the Eu $4f$ band will be bent upward to cross the Fermi level. Therefore, we expect that an important origin of the moment reduction below the Hund's rule moment of $m_{4f} = 7\,\mu_B$ for elemental Eu is that near the interface the Eu $4f$ orbitals are partially depopulated into the Pt capping layers by an upward bending of the conduction band as well as of the Eu $4f$ valence band, such that the latter crosses the chemical potential. The length scale for the range of the band bending is controlled by the charge screening lengths in the EuO conduction and $4f$ bands, i.e. significantly shorter than the range of the RKKY interaction. This is consistent with our experimental finding that the bulk moment is recovered for film thickness $d \geq 6$ nm (Fig. 3), while the bulk T_C is obtained only for thickness $d \geq 40$ nm (Fig. 2). Signatures of a modified surface electronic structure have been reported previously for EuO bulk crystals [25, 26] and possibly thin films [27]. Direct experimental evidence for a significant upward band bending at the Pt-EuO_{1-x} interface can, however, be seen in the temperature dependence of the magnetization shown in the inset of Fig. 2. These magnetization curves are notable for the gradual disappearance of the secondary dome with decreasing film thickness. This dome is always present in the magnetization curves of doped bulk EuO samples [5, 6]; it constitutes a deviation from the Brillouin function of a Heisenberg lattice of localized spins [6] and it is associated with the magnetization of the occupied conduction band [9]. The disappearance of the secondary dome thus indicates a complete depopulation of the EuO_{1-x} conduction band caused by an upward bending above the
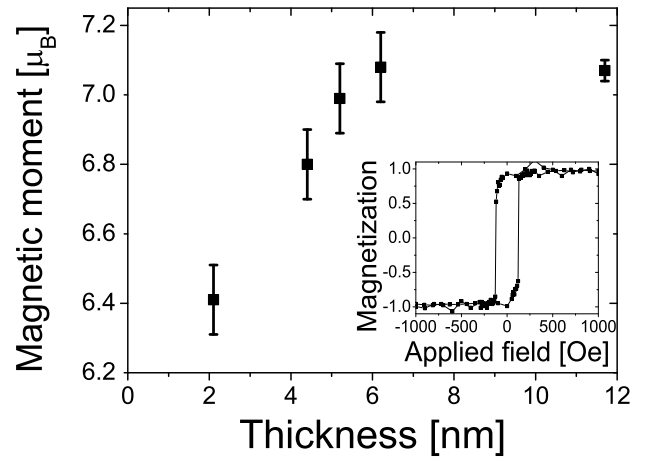

FIG. 3: Magnetic moment of $EuO_{0.96}$ for varying thickness, t_{PNR}=2.1, 4.4, 5.2 and 6.2 nm. The 11.7 nm datapoint is taken from Ref. [6]. The inset shows a hysteresis loop taken by SQUID at 5 K for a 2 nm sample.

chemical potential. Thus, we conclude that surface band bending is the most significant cause for the moment reduction in thin EuO_{1-x} films. The band bending effect due to interface charge transfer can be calculated within a semiclassical Thomas-Fermi theory, where the local interface potential, $V(z)$, and the interface charge density distribution in that potential, $\delta\rho(z)$, are calculated self-consistently using Gauss' law and the locally shifted band energy levels, respectively, and minimizing the total energy of the interface [29].

To conclude, we have performed systematic measurements of the Curie temperature and layer-average magnetic moment in thin, oxygen-deficient EuO films in dependence of the film thickness. These measurements enabled us to study the influence of the film interface on these quantities and to analyze the physical effects contributing to their reduction. In stoichiometric EuO the Curie temperature is reduced for film thicknesses smaller than 10 nm, and we found that this reduction can be well explained semiquantitatively by the reduced number of neighboring magnetic atoms at the surface of the Eu sublattice. In electron doped, i.e., semiconducting $EuO_{0.96}$ there is an overall, numerical enhancement of the Curie temperature with respect to stoichiometric EuO, but the surface-induced reduction extends up to higher film thicknesses of about 40 nm. The overall absolute-value enhancement and the thickness-dependent reduction can both be understood qualitatively in terms of the conduction-electron mediated, long-range RKKY spin-exchange interaction operative in these conducting films. Analyzing the reduction of the layer-average magnetic moment per Eu atom, we found interface-induced band bending and concomitant partial depopulation of the Eu $4f$ band to be the dominant mechanism, besides possible pinning effects. This conclusion was reached by estimating the energy gain for transferring Eu $4f$ electrons at the interface with the Pt capping layers. Our results are also relevant for applications of EuO in spintronics, where interface effects naturally play an important role. Especially, our conjecture that the moment may be controlled by the interface work functions may be useful for maximizing the magnetic moment of EuO in ultrathin layer structures. More detailed, spatially dependent calculations will, however, be needed to understand the reduction of the magnetic moment as well as of the Curie temperature quantitatively.

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